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Modern Cyclophane Chemistry

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Contents

Preface

[2.2]Paracyclophane, first prepared in 1949 by Brown and Farthing and then systematically investigated by Cram and his co-workers from 1951 onward, is now a molecule with a history spanning half a century. A history, however, as confirmed inter alia by this monograph, that is not only active and living, but also increasingly extending into novel fields and applications. This is rare for any organic compound and certainly rare for hydrocarbons (excluding such household chemicals such as natural gas and gasoline).

So, what are the reasons for this unabated interest?

The first reason was already obvious to the pioneer workers in this area: The interaction between layered π-systems combined with an unusual three-dimensional structure. Indeed, most of the early studies in cyclophane chemistry were connected to the problem of the “bent and battered benzene rings” (so the title of a classical review article by Cram) and the consequence this structural feature had on the chemical behavior of the cyclophanes. Obviously, the distance between the aromatic subunits (the “decks”) could be altered by changing the nature of the molecular bridges, and one can say that this classical period of cyclophane chemistry culminated in the preparation of superphane by Boekelheide and certainly with the preparation of [1.1]paracyclophane by Tsuji.

What – secondly – had become more and more obvious during these studies was the realization of what may be called the “phane concept”. Just as benzene is the epitome of a planar (flat) aromatic molecule, [2.2]paracyclophane is the example par excellence of a three-dimensional aromatic molecule. Not only did leaving the π-plane lead to the realization that a new, widely variable class of chiral molecules had become available – with all the effects on, for example, stereoselective synthesis – but the bridged aromatic concept could be connected effortlessly to the simultaneously evolving areas of crown ether, cryptand, cavitand, and supramolecular chemistry. To put it another way: numerous supramolecular structures are cyclophanes (and it may be added in passing that – viewed from this angle – there is also a huge group of naturally occurring cyclophanes).

Thirdly, the zwitter character of the cyclophanes became evident during this period. Whereas, for example, adamantane or cubane are only aliphatic molecules, and benzene or the condensed aromatic systems or even the fullerenes are only (highly) unsaturated compounds, the cyclophanes are both: aromatics and aliphatics (as already indicated by the euphonious name), making the use of both types of chemistries applicable. As far as the aromatic part of the cyclophanes is concerned, this not only meant the application of the typical reactions of classical aromatic chemistry to these compounds, but also the preparation of reactive intermediates derived from the aromatic rings: radical cations, radical anions, etc. Furthermore there was also the unique possibility of combining cyclophane chemistry with the archetypical layered inorganic chemistry, as exemplified by the classics ferrocene and dibenzene chromium. The cyclophanes, however, offer the additional topologically interesting and important possibility of bonding the metal to the interior or the exterior of the organic ligand. Incidentally, the chemical behavior of the molecular bridges in cyclophanes has not been studied to the same extent as the reactivity of the aromatic subunits.

Finally, the crucial test for the significance of a molecular assembly is its practical application. After all, if the properties of a chemical compound are really "interesting", there must also be practical, industrial applications. With the increased use of cyclophanes as monomers for the preparation of new polymers by CVD techniques with unusual and characteristic properties, polymers not just of importance as chemically very stable surfaces, e.g. for printed circuits, but also as new materials for medical application and drug delivery, cyclophanes are finding more and more applications in materials science. Together with their use in all kinds of optical devices, and as ligands in stereoselective synthesis, we are observing a very rich field developing here.

It is our aim with this volume to show these different developments in cyclophane chemistry. That we succeeded was, of course, only possible because we found a group of excellent contributors and cyclophane specialists willing to give us their time and share their knowledge. As far as the practical side is concerned, we are very grateful to Drs. Gudrun Walter, Bettina Bems from Wiley/VCH, Mary Korndorffer for copy editing and Petra Krämer and C. Mlynek for drawing the numerous and often very complex structures.

We dedicate this volume to the memory of Donald Cram and Virgil Boekelheide.

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April 2004

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1
Cyclophynes

Yoshito Tobe and Motohiro Sonoda

1.1
Introduction

The chemistry of cyclophynes having carbon–carbon triple bond bridges has been one of the most actively investigated fields in modern cyclophane chemistry, particularly in connection with the evolving fields of carbon-rich materials and shape-persistent macrocyclic compounds. In accordance with the remarkable progress in this field over the last decade, a number of reviews has already been published based on the authors' own perspectives [1–9]. Since, in this review, the authors wish to provide a comprehensive survey of cyclophyne chemistry, some overlaps are inevitable.

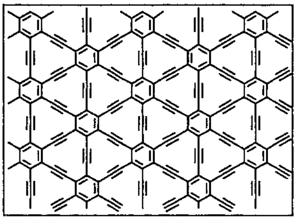
The properties of cyclophynes are characterized by the geometric and electronic properties of triple bonds and the substitution pattern of the aromatic rings. With regard to the geometrical properties, the macrocyclic frameworks of cyclophynes can be expanded by incorporation of triple bonds because of their linearity. The substitution pattern of the aromatic rings, on the other hand, fixes the direction of the bridging triple bonds, defining the whole molecular shape. As a result, a variety of two- and three-dimensional architectures can be built by connecting aromatic rings with triple bond linkages. The ortho substitution pattern would lead to conjugated cyclophynes, also regarded as dehydrobenzoannulenes (DBAs), with either planar or nonplanar shape depending principally on their ring size. Although planar DBAs had been studied extensively during the late 1950s through mid-1970s in connection with the aromaticity/antiaromaticity of annulenes, these are currently being investigated with renewed interest regarding their potential as opto-electronic materials. On the other hand, nonplanar macrocycles of this type have been studied with regard to their conformation, chirality, and their potential application to liquid crystalline and sensing materials. Some highly unsaturated members of this type of compound have been shown to serve as precursors of ordered carbon materials. Since the meta substitution pattern would make the size of the cyclophynes larger than the ortho analogs, keeping the planarity of the macrocyclic rings, a number of shape-persistent metacyclophynes have been synthesized in order to investigate their supramolecular properties such as guest-binding and self-association in solution, solid state, and at solid–liquid and air–liquid interfaces. To form cyclic structures of para substitution pattern, macrocycles adopt a cylindrical shape, and with 1,3,5-trisubstitution, a cage-like structure can be constructed. These three-dimensional molecules have been studied in view of the host–guest chemistry of curved π-systems, strain of triple bonds, and their transformation into all-carbon molecules.

Concerning the electronic properties of C–C triple bonds, acetylene linkages are capable of transmitting electronic perturbation efficiently from one end of conjugated π-systems to the other because of the isotropic distribution of the π electrons along the C–C axis. This characteristic is responsible for the unique opto-electronic properties predicted for planar cyclic compounds like DBAs. Because C–C triple bonds have a high energy content, it is well known that structurally unhindered alkynes react violently, frequently with explosion. Similarly, diynes are known to undergo topochemical polymerization to form poly(butadiyne)s, potential materials with nonlinear optical properties. The high potential of the triple bonds toward spontaneous chemical reactions has been exploited to provide the transformation of some cyclophynes into all-carbon and carbon-rich materials. In addition, because triple bonds serve as good ligands for transition metals, a number of metal complexes of cyclophynes with unique structures has been readily prepared.

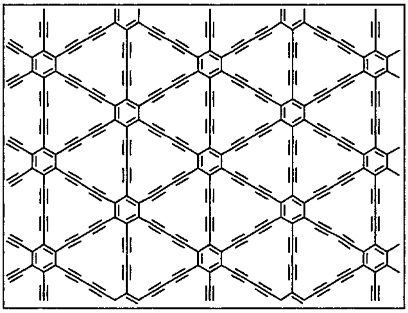
Besides the interest from materials science, recent development of new synthetic methods, particularly those based on transition metal-catalyzed bond formation between sp–sp^2 and sp–sp carbons, have been playing a crucial role in the rapid growth of this field. This chapter covers the recent development of the two- and three-dimensionally shaped cyclophynes from the above points of view. For convenience, the molecules are classified into three types: (1) orthocyclophynes with either planar or nonplanar shape; (2) metacyclophynes; and (3) paracyclophynes and 1,3,5-bridged cyclophynes, on the basis of the substitution pattern. Those compounds with mixed substitution pattern such as ortho, para and meta, para are included in one of the above three types depending on their most characteristic structural and/or functional properties.

1.2
Orthocyclophynes and Related Systems

Fully conjugated planar orthocyclophynes are regarded as dehydrobenzoannulenes (DBAs) [2, 3, 4, 6]. 12-, 14- and 18-membered macrocycles of this type are investigated intensively in connection with their opto-electronic properties, theoretical and experimental inspection of aromaticity, and as substructures of hitherto unknown two-dimensional carbon networks, graphyne and graphdiyne [9]. On the other hand, since the macrocyclic frameworks of larger orthocyclophynes are nonplanar, these molecules are investigated in view of their structure and the chirality of twisted π-systems [7]. In addition, highly unsaturated compounds of this class are studied as possible precursors to nanocarbon materials such as carbon onions and tubes.



Graphyne



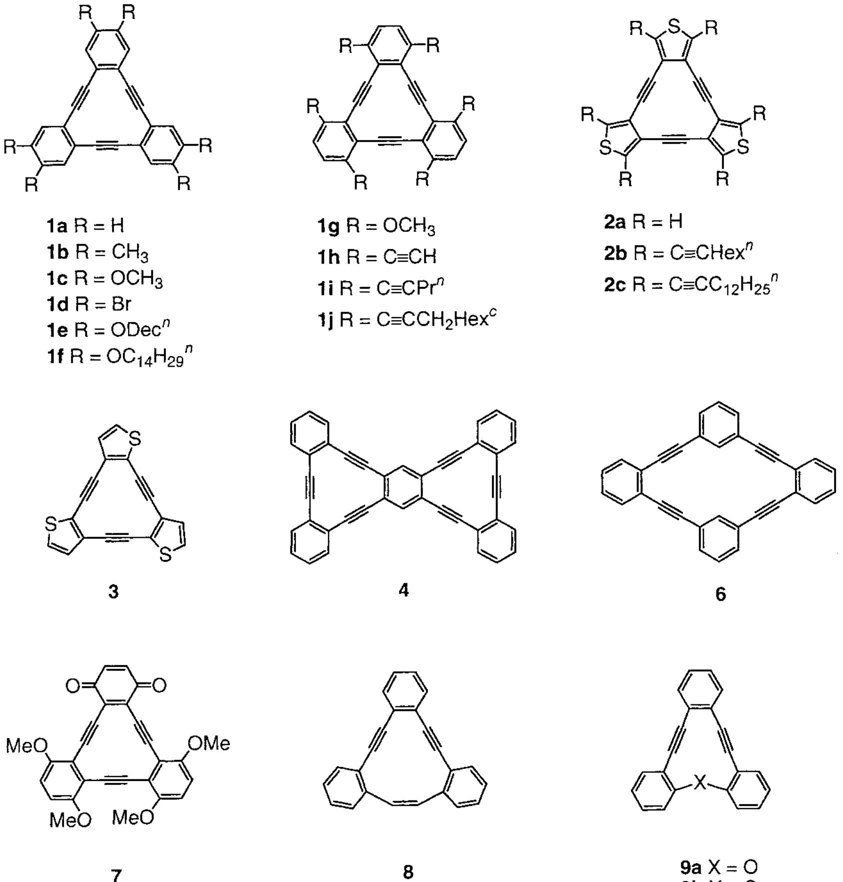
Graphdiyne

Fig. 1.1

1.2.1
Planar Dehydrobenzoannulenes

It was predicted that the two-dimensional carbon network, graphyne, would exhibit semiconductive and nonlinear optical properties [10]. Recent calculations from first principles confirmed that graphyne should be a semiconductor with a moderate band gap and should be quite stable once synthesized [11]. It was predicted that potassium-intercalated graphyne would become metallic with a remarkably short distance (4.30 Å when each 12-membered ring holds a potassium atom) between the intercalant layers [12]. In connection with the nonlinear optical properties of graphyne, hyperpolarizabilities of ladder oligomers of dehydrobenzo[12]annulene ([12]DBA) have been estimated, based on semiempirical calculations, indicating that these can be promising third-order nonlinear optical materials [13]. Force field calculations for networks related to graphdiyne revealed that they would exhibit negative Poisson's ratios, an unusual mechanical property caused by the rotation of triangles [14].

Most cyclophynes were synthesized by using the Stephens-Castro and Sonogashira reactions for the C(sp^2)–C(sp) bond formation or copper(II)-mediated oxidative coupling for C(sp)–C(sp) bond formation. Remarkable improvements in the synthesis of cyclophynes have been achieved as exemplified by the synthesis of the known [12]DBA **1a**. These include (1) the Stephens-Castro reaction of the preformed copper(I) acetylide [15]; (2) one-step synthesis by the Sonogashira coupling using acetylene [16]; (3) selective construction of the 12-membered ring based on a masking/protection protocol for both aryl iodide using dialkyltriazene group and alkyne terminal using trialkylsilyl groups [17]; and (4) the alkyne metathesis method [18], which has been developed recently (Scheme 1.1). The first two methods were also utilized for the synthesis of thiophene analogs **2a** [16] and **3** [19]. By stepwise construction of the requisite precursor followed by intramolecular Sonogashira coupling, Haley synthesized bisDBAs **4** and **5a** [17]. An another derivative of the latter compound **5b** was also prepared by an *in situ* deprotection–cyclization method to prove the theoretical prediction for hyperpolarizability of this sys-



1a R = H
1b R = CH_3
1c R = OCH_3
1d R = Br
1e R = $ODec^n$
1f R = $OC_{14}H_{29}{}^n$

1g R = OCH_3
1h R = C≡CH
1i R = $C{\equiv}CPr^n$
1j R = $C{\equiv}CCH_2Hex^c$

2a R = H
2b R = $C{\equiv}CHex^n$
2c R = $C{\equiv}CC_{12}H_{25}{}^n$

3

4

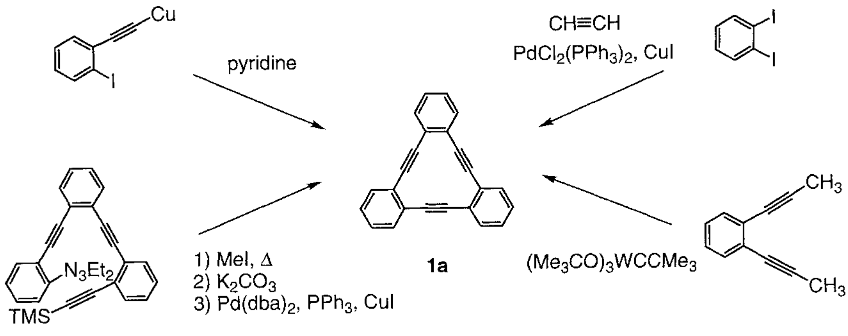
6

7

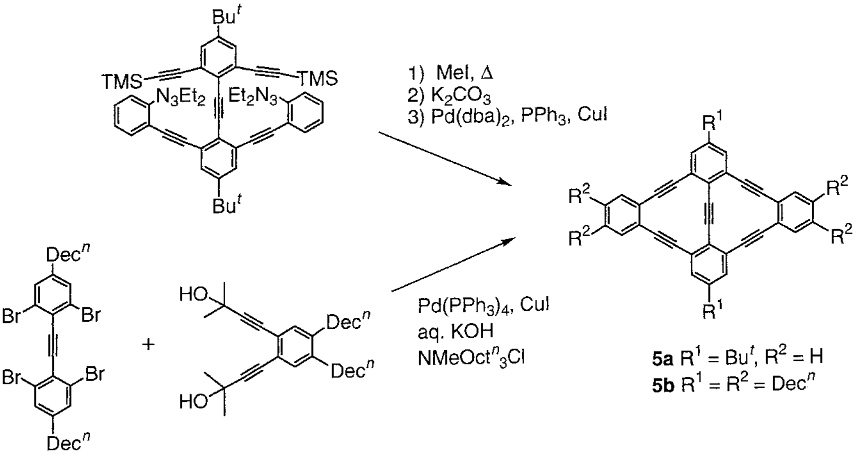
8

9a X = O
9b X = S

Fig. 1.2



Scheme 1.1



Scheme 1.2

tem (Scheme 1.2) [20]. Not only the parent hydrocarbon **1a** but also a number of its derivatives **1b–d** have been prepared by the metathesis method, except for those with substituents adjacent to the alkyne bridges. Similarly, the metathesis method was applied to the synthesis of bisDBA **4** and orthometacyclophyne **6** [18].

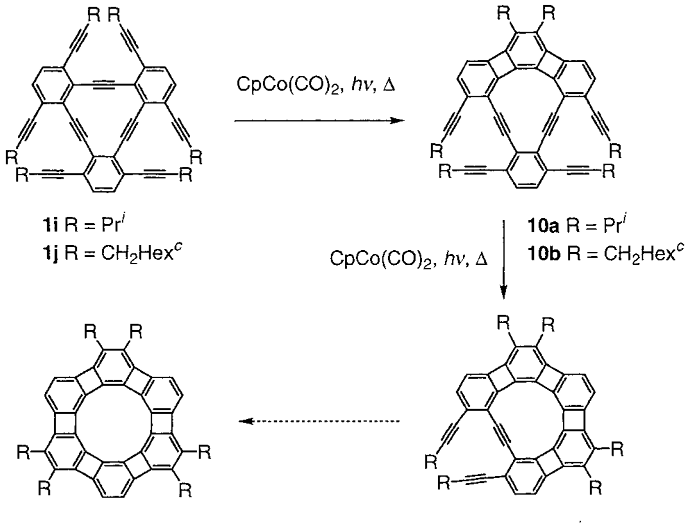
Since the late 1980s, Youngs and Tessier have been developing new frontiers in the chemistry of the [12]DBA system [6]. A number of transition metal complexes of **1a** were prepared such as Co(0), Cu(I), Ag(I), and Ni(0) complexes [21]. Significantly among these metal complexes, the Ni(0) complex becomes semiconductive [22]. For example, the Ni(0) complex doped with potassium [2.2.2]cryptate (1:2 ratio) exhibits conductivity of a moderate semiconductor regime (2×10^{-3} S cm^{-1}). The hexamethoxy derivative **1g**, hexa-alkoxy derivatives **1e–f** having long alkyl chains, and their Ni(0) complexes were also prepared, as well as the quinone **7** and thiophene derivatives **2b–c** [23]. In spite of the expectation based on their structural similarities to hexasubstituted triphenylene derivatives, DBAs **1e–f** and **2b–c** with long alkyl chains did not exhibit liquid crystalline properties.

A dihydro derivative of **1a**, cyclophanediyne **8**, was prepared by Iyoda *et al.* using modified McMurry coupling conditions, followed by dehydroxylation [24]. Although the X-ray structure analysis of **8** revealed its short transannular distance (the shortest C(sp)–C(sp) distance: 2.77 Å), it was inert to photoirradiation. On the other hand, heating **8** at 250 °C in the presence of cyclohexa-1,4-diene resulted in the formation of dibenzonaphthocyclooctatetraene, a product of the Bergman cyclization. The corresponding transannular distances of the oxygen- and sulfur-bridged diynes **9a** and **9b**, respectively, are longer than that of **8** (3.44 and 3.50 Å, respectively), and it is reported that these compounds are inert to thermal and photochemical cyclization [25].

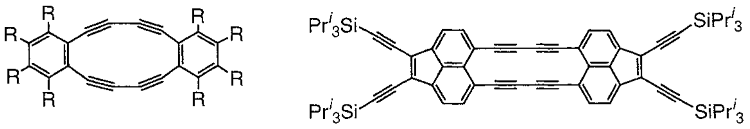
Hexa-ethynyl derivatives **1i–j** were prepared as the key intermediates for the synthesis of antikekulene **12**, an antiaromatic counterpart of kekulene [26]. Thus the first intramolecular CpCo-catalyzed cyclotrimerization of **1i** and **1j** yielded the triphenylene-based cyclophynes **10a** and **10b**, respectively, whose second cycloisomerization furnished the corresponding pentaphenylene-based cyclophynes **11a** and **11b** (Scheme 1.3). The final cyclization to the target **12** is yet to be realized. Besides this spectacular synthetic endeavor, the parent hydrocarbon **1h** was found to form crystals with highly organized channels including tetrahydrofuran induced by multiple alkyne C–H...O hydrogen bonds [27].

Perethynyl-substituted dibenzodehydro[12]annulene **13a** was prepared by Rubin *et al.* by oxidative coupling of a differentially substituted hexa-ethynylbenzene derivative [28]. Hydrocarbon **13a** can be regarded as a constituent unit of a two-dimensional network with different topology from that of graphdiyne and as a monomer of ladder polymers constructed from the dibenzodehydro[12]annulene ring, called acynes. In this connection, Anthony prepared tetra-ethynyl-substituted [14]DBA **14** having acenaphthene units as a possible monomer unit of the related ladder polymers [29]. In connection with the topochemical polymerization of butadiynes, Komatsu *et al.* prepared octafluoro[12]DBA **13c**, whose reduction potential was more negative than that of the parent hydrocarbon **13b** [30]. In the two crystal forms of **13c**, the molecules are stacked in a slanted manner, while in the cocrystal of **13b** and **13c** (1 : 2), the molecules are stacked in a columnar arrangement forming a sandwich-like complex. In spite of the favorable packing geometries for topochemical polymerization, none of the crystals underwent photochemical polymerization, probably because of the high potential energy of the polymerization product.

As a quantitative measure of aromaticity of DBAs, the nuclear independent chemical shift (NICS) values at the center of the macrocyclic ring of **1a**, as well as



Scheme 1.3



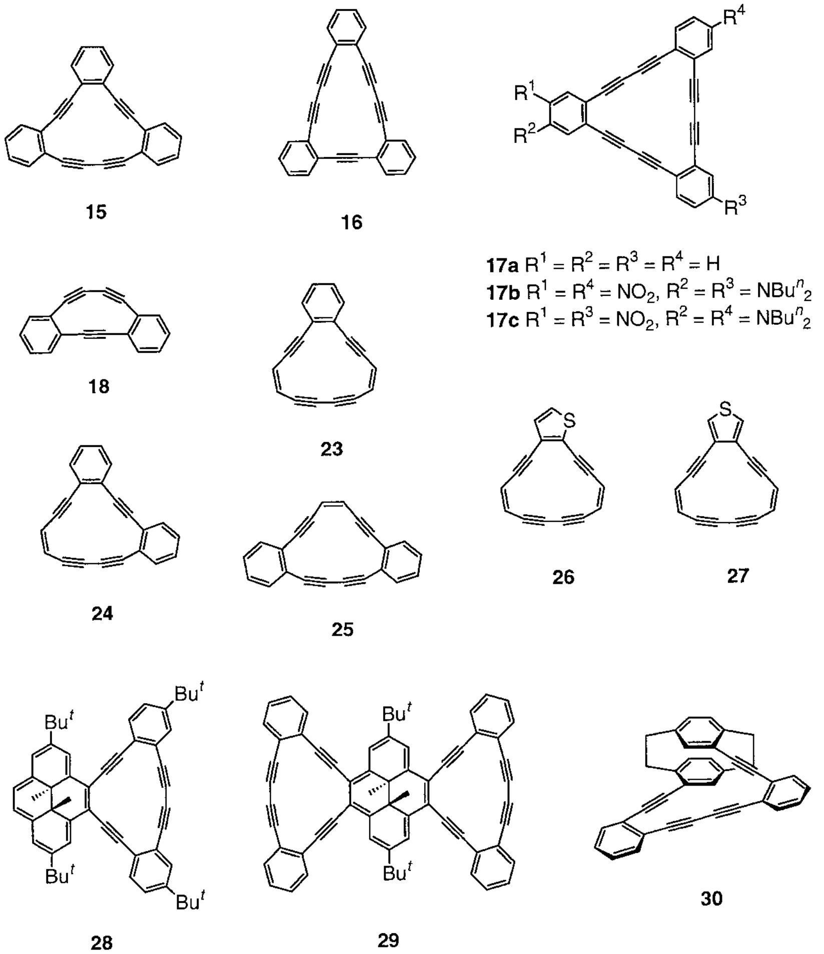
13a R = $C\equiv CBu^t$
13b R = H
13c R = F

14

Fig. 1.3

those for [14]annulene **15**, [16]annulene **16**, and [18]annulene **17a**, were estimated by the DFT method, indicating that **1a** and **16** are moderately antiaromatic while **15** and **17a** are weakly aromatic [31]. Similarly we can predict that highly strained [10]annulene **18** is fully aromatic [31c]. In order to investigate the effect of strain on the tropicity of DBA rings, tetrakisdehydro[12]annulene **19** was generated by photochemical [2+2] fragmentation of the propellane precursor **20** in an argon matrix at low temperature and was characterized by comparison of UV and IR spectra with those calculated by the DFT method (Scheme 1.4) [32]. Unfortunately, since the [12]annulene system **19** was too reactive to observe its tropicity in solution, the next higher homolog **21** was produced by the same method from the homologous precursor **22**. The calculated ^1H NMR chemical shift by the DFT method and experimental observations revealed that strained pentakisdehydro[14]annulene **21** was as diatropic as the corresponding tetrakisdehydro derivative **22**.

Interestingly, the 14-membered DBA ([14]DBA) **15** underwent topochemical polymerization induced by photoirradiation or by applying pressure (20000 psi) [33]. From the packing diagram of the crystal, *trans–trans* geometry of the polymer chain was suggested. This represents the first example of the topochemical polymerization of a conjugated cyclic diyne derivative, although the reactions of acyclic butadiyne derivatives have been well known to form poly(butadiyne)s, which are known to exhibit interesting optical properties. In connection with the theoretical prediction regarding the tropicity of dehydrobenzo[14]annulenes, Haley prepared a number of monobenzo, dibenzo, and monothiopheno derivatives such as **23–27** and studied their diatropicities based on the ^1H NMR chemical shifts [34]. As a result, fusion of a benzene ring to the dehydro[14]annulene ring induces stepwise loss of aromaticity with increasing number of the fused rings. The relative aromaticity (RA) was defined by the chemical shifts relative to those of a non-conjugated reference compound. The experimental RA_{expt} values are in accord with the theoretical values (RA_{NICS}) derived from the calculated NICS values. To further confirm the aromaticity of the [14]annulene system, hybrid systems **28** and **29** formed by fusion of the [14]DBA ring to dimethyldihydropyrene (DHP) unit were prepared [35]. The chemical shift of the probe methyl group in the DHP system of mono-DBA-fused compound **28** was compared with appropriate references. However, the effect of benzoannelation on aromaticity of the [14]DBA ring is not conclusive probably because of the small chemical shift change. Bis-DBA fused system **29** cannot be used for the examination of aromaticity because



15 **16** **18** **23** **24** **25** **26** **27** **28** **29** **30**

17a $R^1 = R^2 = R^3 = R^4 = H$
17b $R^1 = R^4 = NO_2$, $R^2 = R^3 = NBu^n{}_2$
17c $R^1 = R^3 = NO_2$, $R^2 = R^4 = NBu^n{}_2$

Fig. 1.4

the effect of one DBA unit on the DHP probe should counteract that of the other DBA. Since Mitchell *et al.* developed reversible photochemical isomerization of fused DHPs with the corresponding [2.2]metacyclophane systems, the isomerization of **29** was examined, because its absorption band extended to 600–800 nm region, which may be used as “read out” without scrambling of information. However, photochemical isomerization was not successful because the cyclophane form reverts very easily to the starting material **29**. A hybrid system **30** between [14]DBA **15** and [2.2]paracyclophane was synthesized in order to investigate the global transannular delocalization through the overall π system [36]. By comparison of the UV absorption with those of appropriate acyclic reference compounds, it was concluded that **30** sustained π-electron delocalization through the circuit composed of the DBA and [2.2]paracyclophane systems.